Communications to the Editor

Four Cubes and An Octahedron: A Nickel-Sodium Supracage Assembly

Euan K. Brechin, Robert O. Gould, Steven G. Harris,
Simon Parsons, and Richard E. P. Winpenny*

Department of Chemistry
The University of Edinburgh
West Mains Road, Edinburgh, EH9 3JJ, U.K.

Received July 10, 1996

Great progress has been made in designing complex metal arrays, such as helices,[1] grids,[2] rotaxanes,[3] extended frameworks,[4] and catenanes,[5] using rigid ligands to link mononuclear metal centers. If similar strategies were to be applied to link polymetallic centers, then yet more sophisticated architectures can be envisaged. In the longer term, creation of molecular devices based on such systems might prove fruitful, since polymetallic centers can themselves display unusual physical properties and facile electron exchange. Here we report a novel example of a supracage assembly in which four nickel cubanes are linked through a central sodium octahedron. Such a molecular species, where dissimilar polymetallic fragments—in this case one Na_6 and four Ni_4 cages—are linked into a supracage assembly, appears to be unprecedented and illustrates the immense complexity which can be expected from the combination of rigid ligands with polynuclear metal complexes.

Reaction of hydrated nickel chloride (2.1 mmol) with Na(chp) (4.2 mmol, chp = 6-chloro-2-pyridonate) and Na_2(phth) (4.2 mmol, phth = the dianion derived from phthalic acid) in MeOH (30 mL) for 3 days, followed by filtration, evaporation to dryness, and recrystallization from fresh MeOH, gives green crystals in 10% yield after 2 weeks.[6] X-ray analysis[7] reveals an elaborate complex of stoichiometry $[Ni_{16}Na_6(chp)_4(phth)_{10}(Hphth)_2(MeO)_{10}(OH)_2(MeOH)_{20}]$ (**1**, Figure 1). Investigations of this reaction are in progress; however, use of the reactants in the same ratio as found in the product does not produce **1**.

The structure contains four chemically identical Ni_4 units, which are each based on an imperfect Ni_4O_4 cube. Since the complex lies on a 2-fold axis, these cubes comprise two crystallographically equivalent pairs. Within these cubes two of the O-vertices are occupied by μ_3-OMe groups and the third by a μ_3-O-atom, which is derived from either a hydroxide or methoxide group. The fourth vertex is occupied by a μ_2-O-atom from phth, hence leaving one Ni⋯O edge of the cube unmade. A similar reaction, but excluding Na_2(phth), leads to the cage $[Ni_4(OMe)_4(chp)_4(MeOH)_7]$, which features a similar cube with all O-vertices occupied by methoxides.[8] Three of the Ni⋯Ni vectors in **1** are additionally spanned by 1,3-bridging carboxylates derived from phthalates. The nickel sites are all six-coordinate, with geometries slightly distorted from octahedral and the remaining sites occupied by one η^2-chp group and five terminal MeOH ligands per Ni_4 cage. Ni_4 cubes are well-known.[8−10]

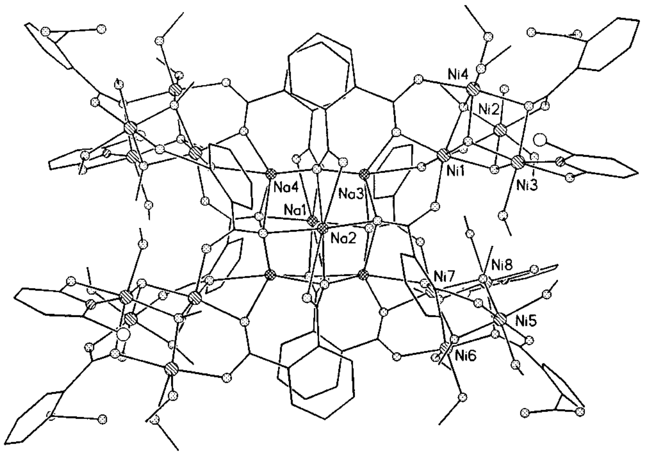

Figure 1. The structure of **1** in the crystal. Bond length ranges (Å): Ni−O(OMe) 1.993−2.095, Ni−O(chp) 2.047−2.052, Ni−O(phth) 1.988−2.141, Ni−O(HOMe) 2.036−2.095, Ni−N(chp) 2.152−2.168, "short" Na−O(phth) 2.252−2.541, "long" Na−O(phth) 2.670−2.725 (average esd of 0.010 Å).

The Ni_4 cages are assembled into a rectangular arrangement through bridging phth groups. The shorter side of the rectangle is bridged by two phth groups, each of which is attached through both O-donors of one carboxylate to one Ni cage and through one O-donor of the second carboxylate to another. The fourth O-atom of this phth μ_3-bridges three Na atoms within the central Na_6 cage. The long edge of the rectangle involves bridging between an Ni_4 unit and the Na_6 cage by one phth group and then a further phth ligand linking out to the next Ni_4 group. Phth bridges have recently been used in the synthesis of Mn_{18}[11] and Co_{13}[12] cages. Four of the phth groups do not bridge between cages but are attached terminally to Ni_4 cubes; charge neutrality requires that on average two of these phthalates are protonated in every assembly.

The Na_6 cage plays a vital structural role, in that all the phth bridges interact with this central motif. The cage is surprisingly regular, with the Na polyhedron close to a perfect octahedron (Na⋯Na contacts vary from 3.59 to 3.85 Å; Na⋯Na⋯Na angles fall within the ranges of 58.7−63.8° or 87.8−90.1°) and with each triangular face capped by a μ_3-O-atom from a phth group. In each case this O-atom is part of a different phth group.

---

[1] (a) Krämer, R.; Lehn, J.-M.; De Cian, A.; Fischer, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 703−706. (b) Constable, E. C. *Tetrahedron* **1992**, *48*, 10013−10059. (c) Potts, K. T.; Keshavarz, M. K.; Tham, F. S.; Abruna, H. D.; Arana, C. R. *Inorg. Chem.* **1993**, *32*, 4422−4435.

[2] Baxter, P. N. W.; Lehn, J.-M.; Fischer, J.; Youinou, M.-T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2282−2287.

[3] Sleiman, H.; Baxter, P.; Lehn, J.-M.; Rissanen, K. *J. Chem. Soc., Chem. Commun.* **1995**, 715−716.

[4] (a) Abrahams, B. F.; Hoskins, B. F.; Michall, D. M.; Robson, R. *Nature* **1994**, *369*, 727−729. (b) Doyle, G. A.; Goodgame, D. M. L.; Hill, S. P. W.; Menzer, S.; Sinden, A.; Williams, D. J. *Inorg. Chem.* **1995**, *34*, 2850−2860.

[5] (a) Fujita, M.; Ibukoro, F.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 4175−4176. (b) Goodgame, D. M. L.; Menzer, S.; Smith, A. M.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 574−575.

[6] Anal. Found: C, 37.6; H, 4.1; N, 1.2. Calcd for **1**: C, 38.6; H, 3.9; N, 1.2.

[7] Crystal data for **1**: monoclinic, $I2$, green blocks, $a = 30.00(2)$ Å, $b = 13.163(9)$ Å, $c = 30.99(3)$ Å, $\beta = 108.83(4)°$, $V = 11\,583(14)$ Å^3, $Z = 2$, $T = 150.0(2)$ K, $R_1 = 0.0917$, GOF = 1.039. Data collection, structure solution and refinement were performed as detailed in ref 8 using the following programs: SHELXS-86, Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473. SHELXL-93, Sheldrick, G. M. University of Göttingen, 1993. PLATON, van der Sluis, P.; Spek, A. L. *Acta. Crystallogr.* **1990**, *A46*, 194−201. Full details have been deposited.

[8] Blake, A. J.; Brechin, E. K.; Codron, A.; Gould, R. O.; Grant, C. M.; Parsons, S.; Rawson J. M.; Winpenny, R. E. P. *J. Chem. Soc., Chem. Commun.* **1995**, 1983−1985.

[9] Paap, F.; Bouwman, E.; Driessen, W. L.; de Graaff, R. A. G.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1985**, 737−741.

[10] Halcrow, M. A.; Sun, J.-S.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1995**, *34*, 4167−4177.

[11] Squire, R. C.; Aubin, S. M. J.; Folting, K.; Streib, W. E.; Hendrickson, D. N.; Christou, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 887−889.

[12] Brechin, E. K.; Harris, S. G.; Parsons, S.; Winpenny, R. E. P. *J. Chem. Soc., Chem. Commun.* **1996**, 1439−1440.

S0002-7863(96)02356-6 CCC: $12.00

The Na_6 core therefore provides eight anchoring points about which to assemble the four tetranuclear nickel fragments. The Na sites fall into two distinct groups: four have five short and one long contacts to O-donors, while the two Na atoms on the 2-fold axis have four short and two longer bonds to oxygens. For all the Na atoms, the coordination geometries are predictably irregular. This type of Na_6 cage is rare, with the only species containing precisely this nuclearity being $[Na_6\{O_2Si(CMe_3)_2\}_6]$, reported by Schutte et al.;[13] octahedral lithium cages are more common.[14]

Preliminary magnetic studies (SQUID susceptometer, Quantum Design) of **1** show a $\chi_m T$ value at 300 K of 19.4 emu K mol^{-1} (χ_m = the molar magnetic susceptibility). At lower temperatures, $\chi_m T$ rises steadily to a maximum of 22.2 emu K mol^{-1} at 20 K, before falling to 18.7 emu K mol^{-1} at the lowest temperature studied (5 K). The distances between the Ni_4O_4 cubes suggest that this behavior must be due to intracube magnetic exchange. For this cube, all spin states between $S = 0$ and $S = 4$ are possible, and given the usually weak exchange between Ni(II) centers, all such states should be populated at room temperature.

For 16 noninteracting Ni(II) centers, $\chi_m T$ would be approximately 19.4 emu K mol^{-1} (assuming $g = 2.2$), similar to the 300 K value for **1**. This confirms that all exchange interactions are weak. The magnetic behavior of Ni_4O_4 cubes has been related to the Ni−O−Ni angles at the μ_2- and μ_3-oxygen bridges,[10] with angles above 99° giving antiferromagnetic (AF) exchange and smaller angles giving ferromagnetic (F) exchange, respectively. Here, the most obtuse bridging angles (117−124°) involve Ni(2) in one crystallographically independent cage and Ni(5) in the second and should lead to the spin at these centers coupling antiferromagnetically with all other spins within the individual cubes, giving an $S = 2$ ground state for each cube. Therefore, if the four cubes do not interact strongly, and the structure suggests they should not, $\chi_m T$ should fall to 15.5 emu K mol^{-1} at low temperature (assuming only the ground state for each cube is occupied and $g = 2.2$). The fall at low temperature is consistent with this prediction. The maximum in $\chi_m T$ at 20 K is explicable if the lowest spin states (i.e., $S = 0$) are highest in energy and hence depopulated as the temperature is lowered before that of the higher spin states (i.e., $S = 4$). Given the correlation of the exchange interactions with Ni−O−Ni angles,[10] this seems likely to be the case. Quantitative analysis of the magnetic data will require further studies.

Acknowledgment. We thank the EPSRC (UK) for funding for a diffractometer and for studentships (for E.K.B. and S.G.H.).

Supporting Information Available: Figure with non-C atoms labeled, details of data collection and structure solution and refinement, and tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates (25 pages). See any current masthead page for ordering and Internet access instructions.

JA962356+

---

(13) Schutte, S.; Klingebiel, U.; Schmidt-Base, D. *Z. Naturforsch. B: Chem. Sci.* **1993**, *48*, 263−269.

(14) Jones, R. A.; Koschmieder, S. U.; Atwood, J. L.; Bott, S. G. *J. Chem. Soc., Chem. Commun.* **1992**, 726−727 and references therein.